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Specific Heat Capacity of Constantan at Low Temperatures[1]

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ABSTRACT

The specific heat capacity at constant pressure of constantan was measured by power-compensated Differential Scanning Calorimeter (DSC) at low temperatures. After the calibration for temperatures and calorimetric sensitivity of the DSC, the optimum heating rate was determined to be $10 K \cdot min^{-1}$ with the measured results of specific heat capacity of synthetic sapphire as a standard reference material. The specific heat capacity of pure copper as a standard reference material was also measured with the optimum heating rate in the temperature range, 97 to 303 K. The uncertainty of the DSC measurements was estimated to be within ± 1 % in this temperature range. Constantan as a negative thermoelement of a J type thermocouple was measured. The 5th order of polynomial correlation for the specific heat capacity of constantan was obtained using least squares. Present results were compared with those of some literatures and also with the specific heat capacities of pure copper and pure nickel.

KEY WORDS: alloy; constantan; differential scanning calorimetry; low temperatures; mixing rule; specific heat capacity; thermocouple materials.

1. INTRODUCTION

The evaluation of heat transfer rate from/to a solid depends on knowledge of a solid's surface temperature. Historically, temperatures have been measured mainly with thermocouples. An accurate evaluation of the surface temperature is often required the heat loss through thermocouples. The specific heat capacity at constant pressure of thermocouple materials must be known for evaluating unsteady heat transfer. Its temperature dependence is also needed in wide temperature range.

One of the authors [1-5] has been developed a new transient calorimetric technique to simultaneously measure the total hemispherical emissivity and the specific heat capacity at constant pressure of metals. The accuracy of this technique mainly depends upon the heat loss through a J type (iron-constantan) thermocouple that suspends a specimen and also measures its temperature. The temperatures of both the specimen and the thermocouple change during the period of measurement, so the calculation of the unsteady state heat loss through a thermocouple requires the values of specific heat capacity at constant pressure of thermoelement materials in wide temperature range.

While the famous Touloukian's data-book [6], the textbook of heat transfer [7] and the manual on the use of thermocouples [8] which include the information of the thermophysical properties of solid materials have been published, the values of specific heat capacity of thermoelement materials in the wide temperature ranges are scarce.

Constantan is a Cu-Ni alloy and a common thermoelement material. To the best of our knowledge, some data have been reported. Eucken and Werth [9] measured the specific heat capacity of constantan using the adiabatic calorimetry in the temperature range, 15 to 202 K. Chemical composition of their constantan is 59.9 wt% Cu, 39.8 wt% Ni and 0.3 wt% other elements. Chung and Brill [10] also reported the values of constantan by an AC calorimetry and a Differential Scanning Calorimetry in the temperature range, 18 to 290 K. This constantan is a negative thermoelement of a E type (chromel-constantan) thermocouple. Its chemical composition is 55 wt% Cu and

45 wt% Ni. They discussed that the specific heat capacities of both constantan with different compositions are in good agreement within 3 % above 70 K. In the temperature range, 380 to 720 K, one of the authors [3] reported recently the values of constantan measured by a new transient calorimetric technique. Its chemical composition is 55 wt% Cu and 45 wt% Ni. At temperature of 293 K, there is only a value [11] for the specific heat capacity of constantan whose composition is 60 wt% Cu-40 wt% Ni.

The purpose of this work is to measure the specific heat capacity of constantan in the temperature range, 100 to 300 K, using a Differential Scanning Calorimeter (DSC). Specific heat capacities of standard reference materials –synthetic sapphire and pure copper- are also measured to determine the optimum heating rate of the DSC and to estimate an accuracy of the DSC at low temperatures. Results of the specific heat capacity of constantan are compared with those of some literatures and also with the specific heat capacities of pure copper and pure nickel.

2. MEASUREMNTS

2.1. Constantan

Constantan is a Cu-Ni alloy [12]. It usually contains small amounts of elements for control of thermal electromotive force, with the corresponding reduction of the nickel or copper. In this work, constantan as a negative thermoelement of a J type (iron-constantan) thermocouple was used. Thermocouple manufactured by Omega Engineering Inc., Stamford, U.S.A. was used as Chung and Brill [10] did. Composition of this constantan is 54.6 wt% Cu, 44.0 wt% Ni, 0.71 wt% Mn, 0.38 wt% Fe, <0.002 wt% Si, 0.0008 wt% S, 0.0020 wt% C, and 0.3052 wt% others. Chemical analysis of this constantan was done in Analytical Laboratory of the Research Institute for Iron, Steel and other Metals, Tohoku University in Sendai, Japan. The measured density of this constantan is 8890 $kg \cdot m^{-3}$.

2.2. Apparatus

A power-compensated Differential Scanning Calorimeter (DSC-7, The Perkin-Elmer Co., U.S.A.) is used to measure the specific heat capacity of constantan and other solid materials. This DSC has reference and sample cells made of platinum-iridium alloy. These cells with a heater and a thermometer are mounted in an aluminum heat sink that is remained nearly at the temperature of cooling bath. In our measurements, this heat sink was always cooled with liquid nitrogen for sub-ambient operation. The level of liquid nitrogen is kept constant in the DSC measurements. Helium, as a purge gas, is constantly passed through the heat sink and over the cells. Aluminum pan containing a sample or a reference material is covered with aluminum cover. Pan and cover are crimped with a special tool. This crimped sample pan is placed in a cell, and a crimped empty pan is also placed in the other cell. Synthetic sapphire (α-Al_2O_3) supplied by the manufacturer and high purity copper are used as standard reference materials. A Mettler AE163 submicrobalance (resolution $\pm$ 0.01 mg) is used to weigh pans, covers, and solid materials. Selecting a pan and a cover with different masses, the mass difference of a set of crimped pans used for measurements is adjusted to reduce to zero. For accurate measurements, the masses of sample and reference materials were carefully determined.

2.3. Procedure

Detailed procedures for using the DSC are described in the literature [13-16]. After the adjustments of isothermal base line and the reductions of the noise level, the DSC for the heat capacity measurement was initially calibrated for temperature and calorimetric sensitivity. Temperature calibration was accomplished using the melting points of indium and cyclohexane, and the calorimetric sensitivity was determined using the enthalpy of fusion of indium. Then, the specific heat capacity of synthetic sapphire as standard reference material was measured with various heating rates over temperature intervals, 100 K, and the optimum heating rate for a DSC measurement was accurately determined. To estimate an accuracy of the DSC at low temperatures,

the specific heat capacity of high purity copper as standard reference material was measured with optimum heating rate. Finally, the specific heat capacity of constantan was measured at low temperatures. The output signals of the DSC are transfer to the Perkin-Elmer 1020 Thermal Analysis Systems and processed to obtain the specific heat capacities of materials with special software.

3. RESULTS AND DISCUSSION

3.1. The optimum heating rate of DSC

To determine the optimum heating rate of the DSC, the specific heat capacity of synthetic sapphire (4.49 mg) as a standard reference material was measured with heating rates ranging from 5 to 20 $K \cdot min^{-1}$ over temperature intervals, 100 K. Heat sink was cooled with ice water only in this measurement, because this DSC is designed to have a good performance above room temperature.

Figure 1 shows the results measured in the temperature range, 330 to 420 K. Excluding the effects of scanning both start and end of DSC, the values measured with heating rate of 10 $K \cdot min^{-1}$ (0.167 $K \cdot s^{-1}$), represented by the symbol ○, are agreed with the recommended values within ± 3 %. Then, optimum heating rate of this DSC was determined to be 10 $K \cdot min^{-1}$, which is also the design value given by manufacturer. This heating rate of 10 $K \cdot min^{-1}$ is always used in all DSC measurements in this work.

3.2. Specific heat capacity of copper

To estimate an accuracy of the DSC at low temperatures, the specific heat capacity of copper (99.991 wt% up purity, polycrystal) as standard reference material was measured with optimum heating rate of 10 $K \cdot min^{-1}$ over temperature intervals, 60 K. Each scanning interval was overlapped about 10 K. Heat sink was cooled with liquid nitrogen in the measurements. Copper sample of 42.65 mg was obtained by mechanically flattening a wire with 0.5 mm in diameter. It was completely annealed at about 780 K for 0.5 hours in a vacuum chamber of about 2×10^{-4} Pa.

Figure 2 shows the measured results of each scanning, Heating 1-4, in the

temperature range, about 90 to 300 K. Results obtained in each scanning start, about over 10 K were omitted. In this figure, the measured results are compared with a solid line that is a smoothed value [17] of the data reported by Martin [18]. Martin measured the specific heat capacity of a single crystal copper with 99.997 wt% up purity using an adiabatic calorimetry. This Martin's data seems to be most accurate at present time. Our results are in good agreement with Martin's data near the room temperatures. But the differences between both values increase at low temperatures, and the maximum difference is higher about 8 % at 100 K.

To check these differences, we again measured the specific heat capacity of copper using the same sample pan. First, to study the effects of the heating scan or cooling scan of the DSC measurements, DSC was scanned with cooling rate of 10 K·min^{-1} in the same temperature ranges. The differences from Martin's data are represented by the symbol △ in Fig.3. It is shown that the differences with cooling scan are higher about 3 % than those with heating scan, the symbol ○. Second, to study the effect of the scanning rate at low temperatures, DSC measurements were repeated with another heating rate of 5 K·min^{-1}. Result shown by the symbol □ in Fig.3 are lower about 3 % than those with heating rate of 10K·min^{-1}, the symbol ○. From these facts, we concluded that this DSC has characteristics to measure higher the specific heat capacity of metals at low temperatures under the conditions we used.

All data shown by the symbol ○ in Fig.3 are again plotted in Fig.4, and were fit with a logarithmic expression by least squares. The solid line in this figure is shown as follows,

$$c_p = 38.939 - 15.802 \log (T) \quad \text{kJ·kg}^{-1}\text{·K}^{-1} \quad \text{for} \quad 97\ \text{K} < T < 303\ \text{K} \qquad (1)$$

If the specific heat capacities of another metals are measured using this DSC under the same scanning and operating conditions at low temperatures, and the measured data should be corrected with above equation (1), then we can obtain the

accurate values of specific heat capacities of another metals. The uncertainty of this DSC measurements for the specific heat capacities of metals is estimated to be within ± 1 % in the temperature range, 97 to 303 K in Fig.4. The value of this uncertainty may be reasonable when compared with detailed descriptions of the accuracy of DSC measurement [19].

3.3. Specific heat capacity of constantan

The constantan sample is a square thin plate with about 0.1 mm in thickness. It was obtained by mechanically flattening a 1/4 inch-diameter constantan bar, and was completely annealed at 780 K for 3 hours in a vacuum chamber of about 2×10^{-4} Pa. The sample mass of this constantan is 36.64 mg.

Specific heat capacity of constantan was measured with optimum heating rate of 10 K·min^{-1} over temperature intervals, 50 K. Each scanning interval was overlapped by about 10 K. Results obtained in each scanning start, over about 10 K were omitted. Heat sink was cooled with liquid nitrogen in the measurements.

Figure 5 shows the measured results of eight scanning, named Runs 1-8, in the temperature range, 95 to 420 K. The data of Runs 1-5 in temperature range, 100-300 K is smoothly connected. Therefore, It seems to be a result of appropriately manipulating DSC. The data of Runs 6-8 above 300 K was also illustrated, but it is not smoothly connected. It is true from the concept of DSC design that the liquid nitrogen cooling should be used for the DSC measurements below room temperatures. Then we excluded the data of Runs 6-8 above 300 K in the present discussion.

The corrected data of Runs 1-5 with equation (1) are shown by the symbol ○ in Fig. 6. These data are correlated with the following 5th order of polynomial equation using least squares. The correlation for specific heat capacity of constantan is obtained as follows,

$$c_p = -0.647+0.01958T-1.688 \times 10^{-4}T^2+7.68 \times 10^{-7}T^3-1.771 \times 10^{-9}T^4 + 1.631 \times 10^{-12}T^5 \quad \text{kJ·kg}^{-1}\text{·K}^{-1} \quad \text{for} \quad 97\ \text{K} < T < 303\ \text{K} \qquad (2)$$

In Fig.6, the solid line is a correlation line plotted from the results given by Chung and Brill [10]. In all temperature ranges, our results are smaller than that of Chung and Brill and the maximum difference is within 3.2 %. The composition of constantan used by Chung and Brill is almost the same composition as ours. The data obtained by AC calorimetry are normalized to values at 200 K determined by DSC, then our results seems to be in good agreement with the data given by Chung and Brill. The specific heat capacity of constantan cited from a textbook of heat transfer written by Eckert and Drake, Jr. [11] is shown as the symbol △ at 293 K in Fig.6. This value taken from Koch [20] is about 4 % higher than our corresponding datum. Composition of this constantan is 60 wt% Cu-40 wt% Ni. Data obtained by Eucken and Werth [9] in the temperature range, 15 to 202 K are not shown in Fig.6. Those are higher than our results, and a largest difference is about 5 %. Composition of this constantan is 59.9 wt% Cu, 39.8 wt% Ni and 0.3 wt% other elements. Long and short broken lines indicate the specific heat capacities of pure copper [17] and nickel with 99.98 wt% purity [21], respectively. Both lines are crossed at near 140 K. Present results are near the copper data above this temperature, and also near the nickel data below this temperature. The calculated values of specific heat capacity of a 55 wt% Cu-45 wt% Ni alloy using a mixing rule of additive properties for specific heat capacity are about 3-5 % higher than present results in all temperature ranges. Similarly, data of Chung and Brill are also 0.5-3 % lower than the calculated values using a mixing rule of additive properties.

4. CONCLUSIONS

The specific heat capacity at constant pressure of constantan was measured at low temperatures, using a Differential Scanning Calorimeter. The specific heat capacity of copper as standard reference material was measured with the optimum heating rate of 10 $K \cdot min^{-1}$. The uncertainty of the DSC measurements was estimated to be within

1 % in the temperature range, 97 to 303 K. Constantan as a negative thermoelement of a J type thermocouple was measured. The 5th order of polynomial correlation for specific heat capacity of the constantan was obtained using least squares. Present results were compared with those of other literatures and also with the specific heat capacities of pure copper and pure nickel.

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FIGURE CAPTIONS

Fig. 1. Deviations of measured specific heat capacity of synthetic sapphire from recommended values with different heating rates

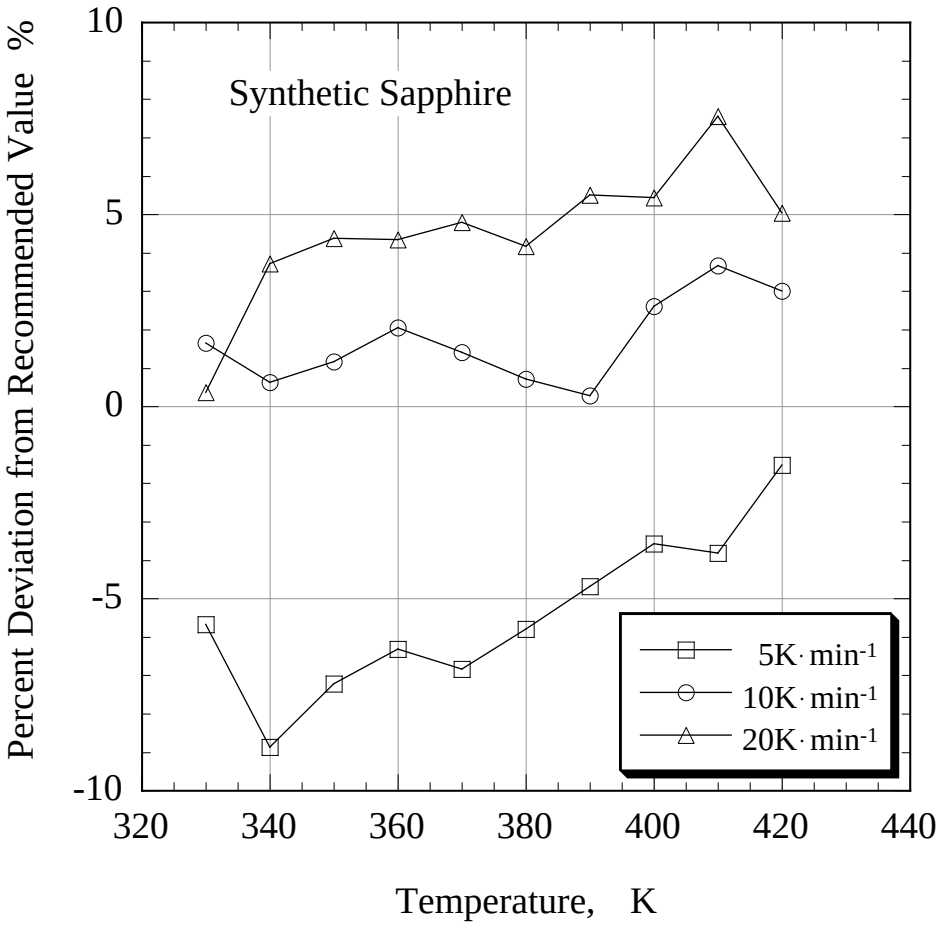
Fig. 2. Specific heat capacity of copper as a function of temperature

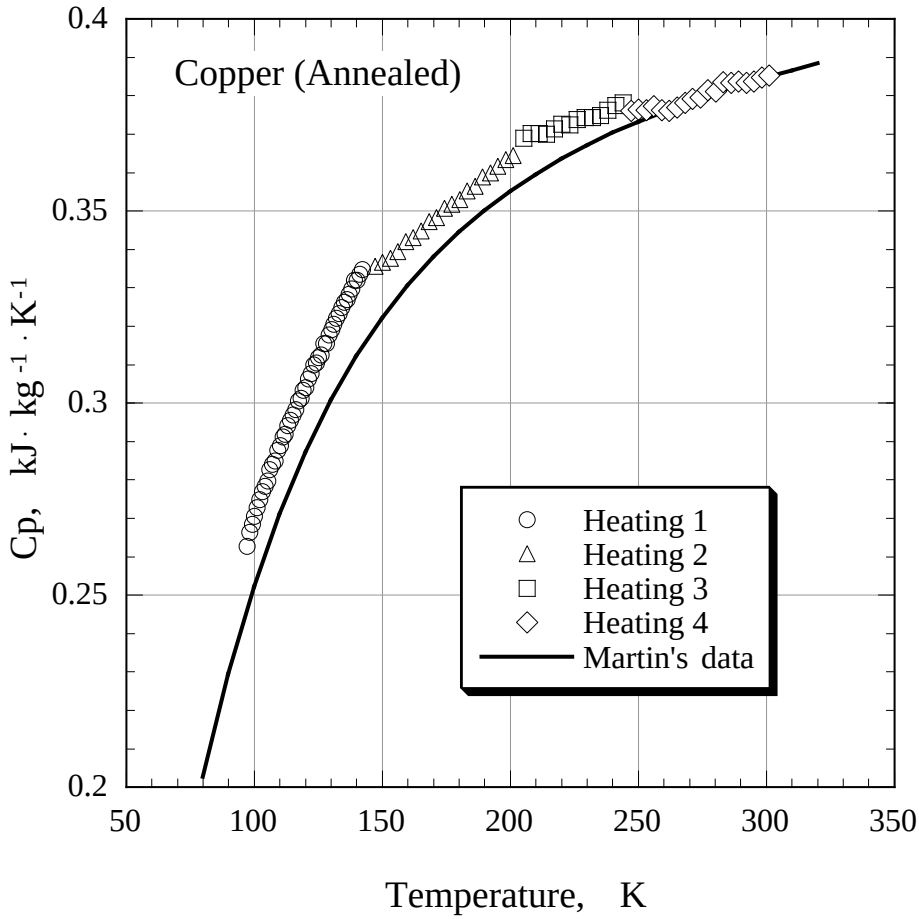
Fig. 3. Deviations of measured specific heat capacity of copper from Martin's smoothed values with different heating/cooling rates

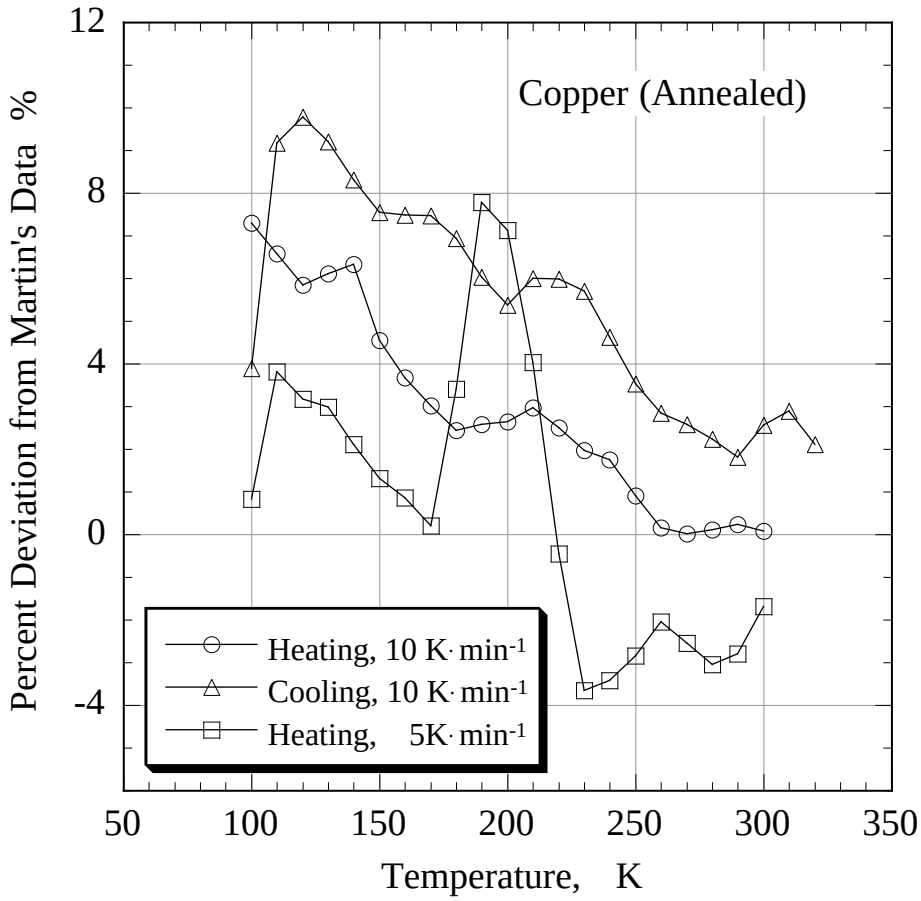
Fig. 4. Deviations of measured specific heat capacity of copper from Martin's smoothed values with optimum heating rate

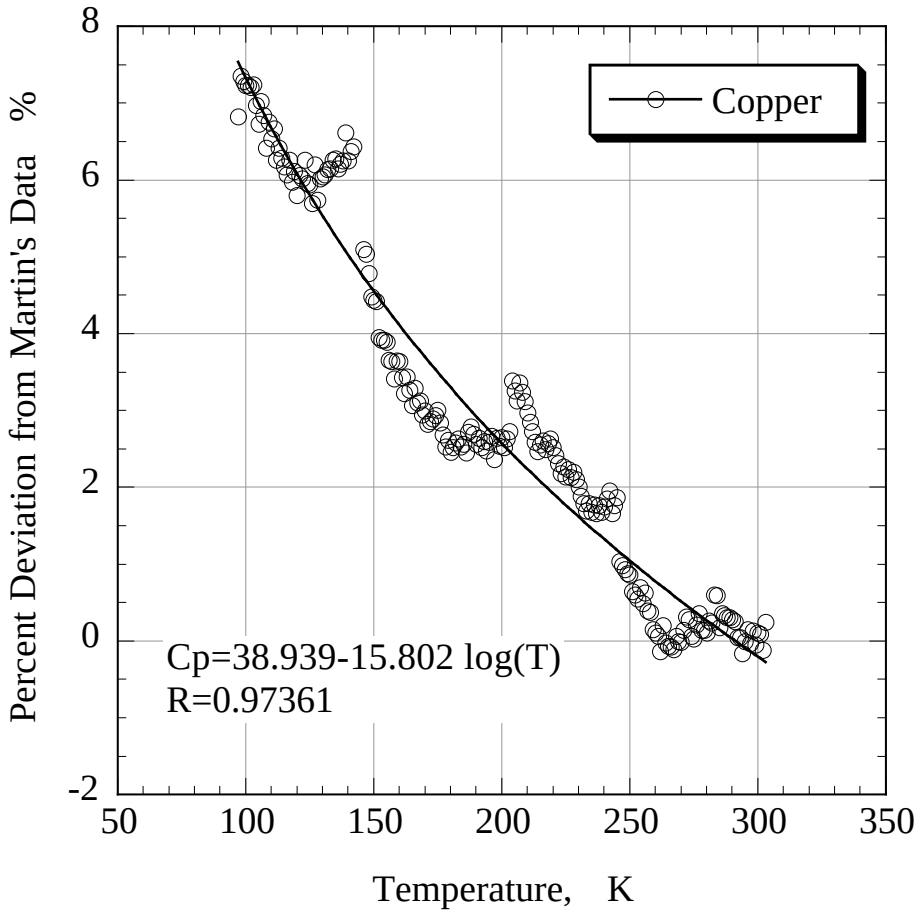
Fig. 5. Specific heat capacity of constantan as a function of temperature

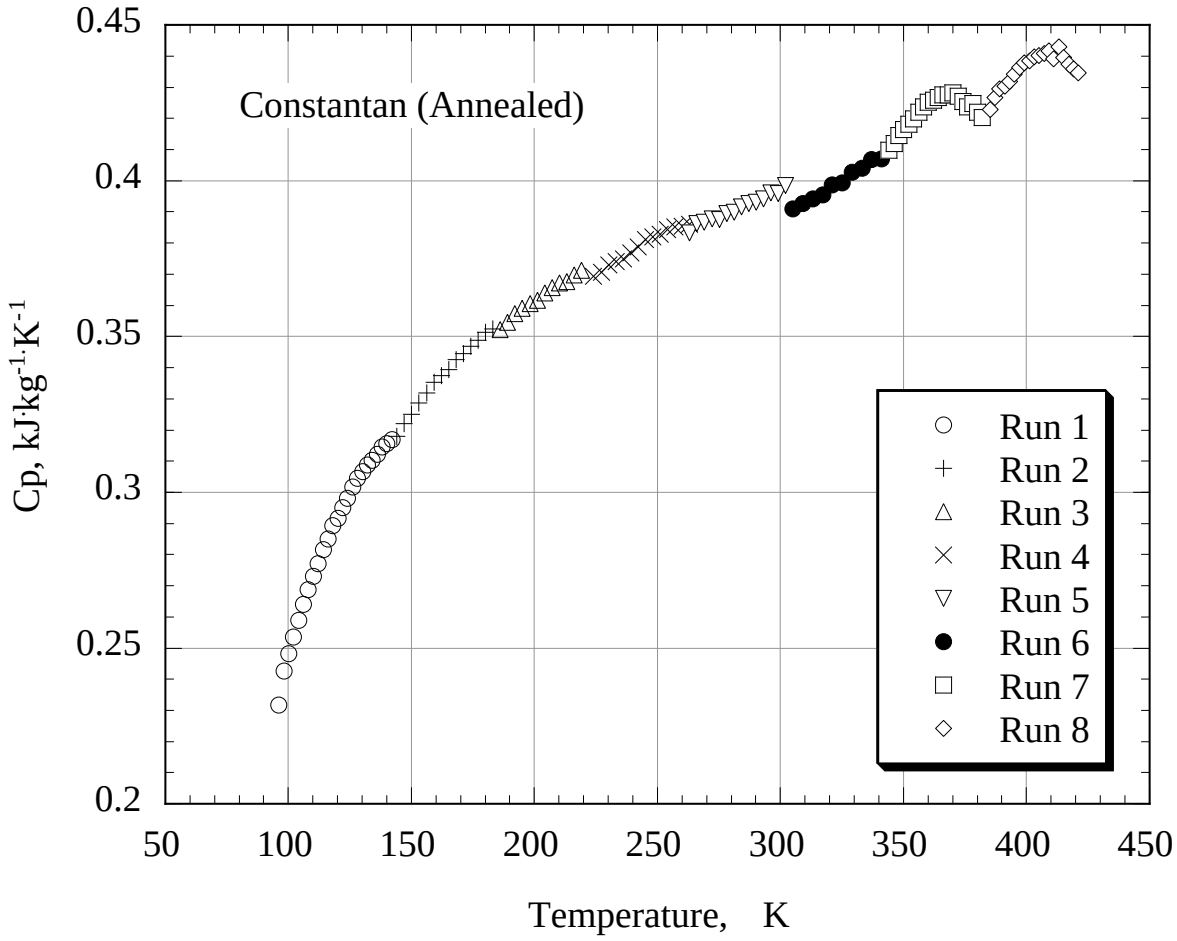
Fig. 6. Comparisons of specific heat capacities of constantan, copper and nickel as a function of temperature

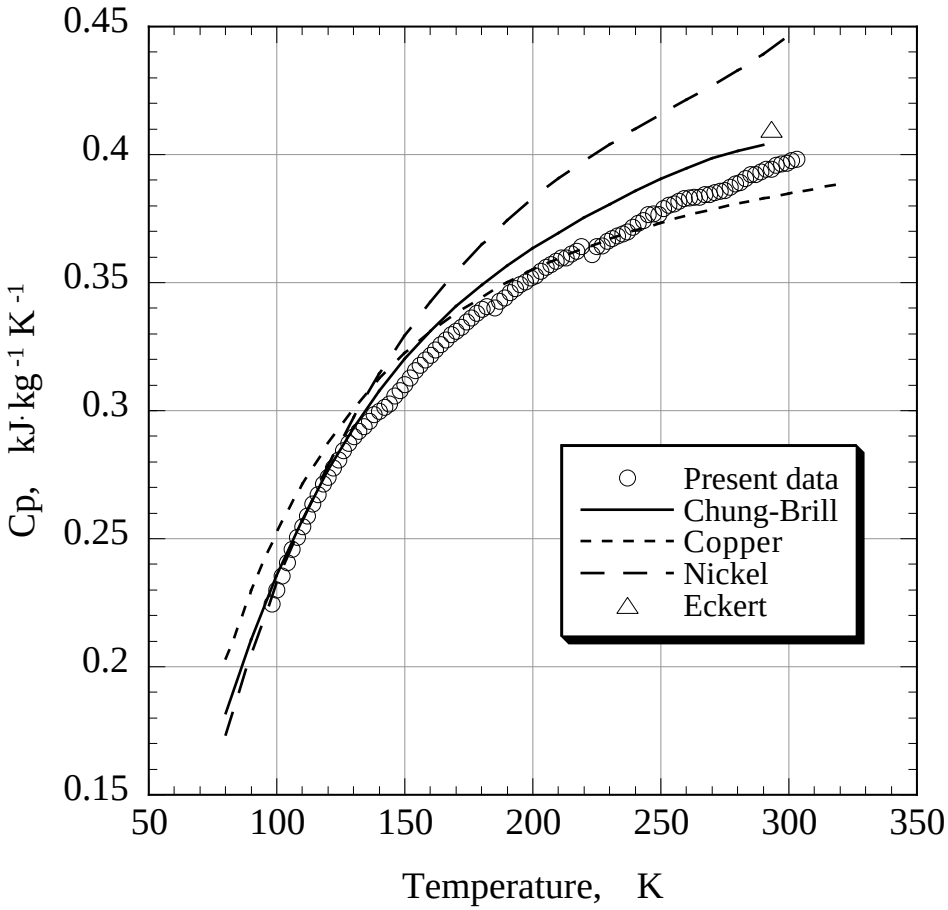

Synthetic Sapphire
Percent Deviation from Recommended Value %
10
5
0
-5
-10
320
340
360
380
400
420
440
Temperature, K
5K·min-1
10K·min-1
20K·min-1


Copper (Annealed)
Heating 1
Heating 2
Heating 3
Heating 4
Martin's data
Cp, kJ · kg -1 · K-1
Temperature, K
0.4
0.35
0.3
0.25
0.2
50
100
150
200
250
300
350


Copper (Annealed)
Percent Deviation from Martin's Data %
Temperature, K
12
8
4
0
-4
50
100
150
200
250
300
350
Heating, 10 K·min-1
Cooling, 10 K·min-1
Heating, 5K·min-1


Copper
Cp=38.939-15.802 log(T)
R=0.97361
Percent Deviation from Martin's Data %
Temperature, K
8
6
4
2
0
-2
50
100
150
200
250
300
350


Constantan (Annealed)
Cp, kJ·kg-1·K-1
Temperature, K
0.45
0.4
0.35
0.3
0.25
0.2
50
100
150
200
250
300
350
400
450
Run 1
Run 2
Run 3
Run 4
Run 5
Run 6
Run 7
Run 8


0.45
0.4
0.35
0.3
0.25
0.2
0.15
Cp, kJ·kg-1 K-1
50
100
150
200
250
300
350
Temperature, K
Present data
Chung-Brill
Copper
Nickel
Eckert